

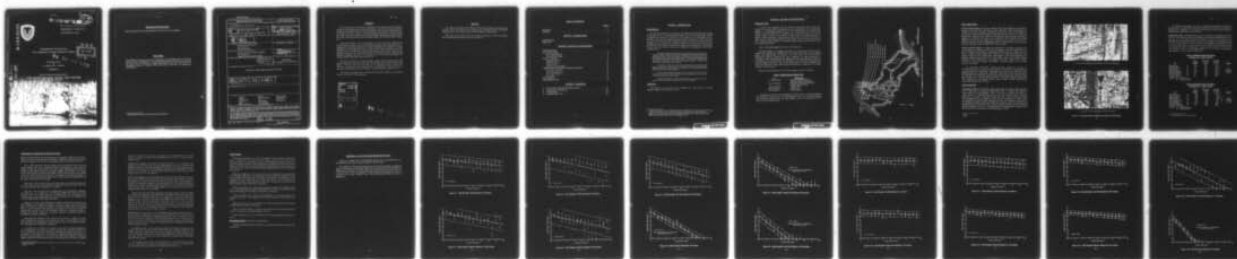
AD-A054 969

ARMY TROPIC TEST CENTER APO NEW YORK 09827
F/G 11/6
METHODOLOGY INVESTIGATION. STEEL CORROSION IN TROPIC MANGROVE F--ETC(U)
NOV 75 M A JOHNSON, G F DOWNS
USATTC-7511002

UNCLASSIFIED

NL

1 OF 1
AD
A054969



END

DATE

FILMED

7-78

DDC

AD A 054969



FOR FURTHER TRAN

AD

TECOM PROJECT NO. 7 CO RD5 TT1 016

USATTC REPORT NO. 7511002

DDC

JUN 13 1978

METHODOLOGY INVESTIGATION:

STEEL CORROSION IN TROPIC MANGROVE FORESTS

78 06 12 139
TECHNICAL NOTE

By

M. A. JOHNSON and G. F. DOWNS III

NOVEMBER 1975

Approved for public release; distribution unlimited.

UNITED STATES ARMY TROPIC TEST CENTER

FORT CLAYTON, CANAL ZONE



DC FILE COPY

DISPOSITION INSTRUCTIONS*

Destroy this report when no longer needed. Do not return it to the originator.

DISCLAIMER

The findings in this report are not to be construed as an official Department of the Army position, unless so designated by other authorized documents. The use of trade names in this report does not constitute an official endorsement or approval of the use of such commercial hardware or software. This report may not be cited for purposes of advertisement.

*These disposition instructions do not apply to the record copy (AR 340-18).

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER TECOM PROJECT NO. 7 CO RD5 TT1 016	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) 6 <u>METHODOLOGY INVESTIGATION</u> <u>STEEL CORROSION IN TROPIC MANGROVE FORESTS</u>	9 <u>TYPE OF REPORT & PERIOD COVERED</u> <u>TECHNICAL NOTE</u> <u>SEPTEMBER 1973-MAY 1974</u>	
7. AUTHOR(s) 10 <u>M. A. JOHNSON</u> <u>G. F. DOWNS, III</u>	6. PERFORMING ORG. REPORT NUMBER USATTC REPORT NO. 7511002	
9. PERFORMING ORGANIZATION NAME AND ADDRESS US ARMY TROPIC TEST CENTER ATTN: STETC-TD APO NEW YORK 09827	8. CONTRACT OR GRANT NUMBER(s)	
11. CONTROLLING OFFICE NAME AND ADDRESS US ARMY TEST AND EVALUATION COMMAND ATTN: DRSTE-ME ABERDEEN PROVING GROUND, MD 21005	10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS	
12. REPORT DATE 11 <u>NOVEMBER 1975</u>	13. NUMBER OF PAGES 31	
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) 12 <u>28 p.</u>	15. SECURITY CLASS. (of this report) UNCLASSIFIED	
15a. DECLASSIFICATION/DOWNGRADING SCHEDULE		
16. DISTRIBUTION STATEMENT (of this Report) Approved for public release; distribution unlimited.		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) 14 <u>USATTC-7511002</u>		
18. SUPPLEMENTARY NOTES		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number)		
Canal Zone Corrosion Dry season, tropic Exposure sites Metals Mangrove exposure sites	Mangrove Materials deterioration Steel Tensile strength Test methodology Tropic exposure sites	Tropic site severity Tropic Test Center Tropic testing Wet season, tropic
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) USATTC in September 1973 exposed 1440 steel samples for 8 months at eight sites (seven mangrove and one coastal) throughout the Canal Zone. Objective was to determine the relative severity of selected mangrove swamps on the corrosion of steel. This study reports the degradation rates of steel samples as measured by tensile strength loss, ranks results by season, and statistically compares results from each exposure site. There were statistical differences between wet and dry season exposures and between Pacific and Atlantic mangrove sites. There was a high degree of correlation between tensile strength loss and conductivity of water run-off collected from mangroves at a given site. High conductivity was caused primarily by water soluble salts washed off the mangroves by rain. One site proved more severely corrosive in both seasons than all others. Salt concentrations in the leaves at the most severe site were three to 16 times greater. It appears that the increased severity in degradation at this site was more a function of exuded salt from the mangroves than salt spray from the ocean. 042 2.90		

SUMMARY

The US Army Tropic Test Center in September 1973 exposed a total of 1440 steel samples for an 8-month period at eight (seven mangrove and one coastal) sites throughout the Panama Canal Zone during the wet and dry seasons. The objective of this project was to determine the relative severity of selected mangrove swamps on the corrosion of steel. This study reports the degradation rates of steel samples as measured by tensile strength loss, ranks the results by season, and statistically compares the results from each exposure site.

Statistical differences were found between wet and dry season exposures and between mangrove exposure sites on the Pacific and Atlantic sides of the Canal Zone. A high degree of correlation existed between tensile strength loss and conductivity of water collected run-off from mangrove trees at a given site. The high conductivity was caused primarily by water soluble salts washed off the mangrove trees by rain. These salts are deposited on the trees by coastal winds as well as by exudation from the mangrove trees themselves. Mangrove forests are not universally severe to steel and must therefore be selected carefully in planning tropic exposure tests.

One site was found to be more severely corrosive than all other sites in both seasons. Analysis of leaves from all mangrove sites showed that salt concentrations in the leaves at the most severe site were three to 16 times greater than in other sites. Therefore, it appears that the increased severity in degradation at this site was more a function of the exuded salt from the mangrove trees than salt spray from the ocean.

This Center recommends that a Test Operations Procedure (TOP) not be developed based on the results of this investigation.

ACCESSION for	
NTIS	White Section <input checked="" type="checkbox"/>
DDC	Buff Section <input type="checkbox"/>
UNANNOUNCED	<input type="checkbox"/>
JUSTIFICATION.....	
BY.....	
DISTRIBUTION/AVAILABILITY CODES	
Dist.	AVAIL. AND/OR SPECIAL
A	

78 06 12 139

PREFACE

The authors are indebted to Dr. William A. Dement and Dr. James F. Sprouse of the US Army Tropic Test Center staff for classification of mangrove species, and chemical analysis of water run-off samples taken within the mangrove exposure sites.

This study was conducted under the technical supervision of Dr. D. A. Dobbins, Chief, Technical Division, US Army Tropic Test Center.

TABLE OF CONTENTS

	<u>PAGE</u>
SUMMARY	1
PREFACE	2

SECTION 1. INTRODUCTION

BACKGROUND	5
OBJECTIVE	5

SECTION 2. DETAILS OF INVESTIGATION

EXPOSURE SITES	7
DATA COLLECTION	9
Steel Tensile Strength	9
Water Run-Off Samples	9
DATA ANALYSES	9
Degradation Model	9
Degradation Rate	11
Expected Life	12
Analysis of Water Samples	13
VARIATIONS IN EXPOSURE SEASONS AND SITES	14
Wet versus Dry Season	14
Galeta Point Mangrove	15
Coco Solo Mangrove A	15
Pacific Sites	15
CONCLUSIONS	16
RECOMMENDATION	16

SECTION 3. APPENDICES

A DATA PLOTS AND PREDICTIONS CURVES	A-1
B STATISTICAL FORMULAE	B-1
C REFERENCES	C-1
D DISTRIBUTION LIST	D-1

SECTION 1. INTRODUCTION

BACKGROUND

In a previous methodology investigation, *Determination of Optimum Tropic Storage and Exposure Sites*,^{1,2} several materials commonly used in Army materiel were exposed at selected sites within the Canal Zone. The purpose of the investigation was to determine the severity of storage and exposure sites for acceleration of tropic tests. Steel was one of the materials exposed during the project. A total of 16 sites were chosen for investigation, one of which was a mangrove swamp site located at Coco Solo on the Atlantic side of the Isthmus of Panama. According to the excerpt below,² this mangrove site was found to be the most severe of all locations for the degradation of the tensile strength of steel:

The mangrove swamp, an experimental site, was the most severe for deterioration of steel. The major deterioration causing factors were unknown. Humidity and salt content in the swamp were comparable to other sites, but the deterioration rate was much greater. The obviously corrosive and strong oxidizing ambient conditions in the mangrove swamp were unique and unparalleled by other subenvironments studied during this investigation. Figure . . . shows the high rate of tensile strength loss measured in steel specimens at the mangrove site during the rainy season . . . Complete loss of tensile strength occurred within 4 weeks of exposure.

The Atlantic and Pacific sides of the Isthmus provided exposure modes and sites equally severe on a representative cross section of types of materials, except for steel. (Steel attained its highest degradation at an Atlantic mangrove site, and could not be compared because no Pacific mangrove site was included in the investigation.)

One of the major findings of this study was that the most severe test site for steel was the mangrove swamp. Deterioration at the mangrove site was accelerated by at least a factor of two over the next most severe site at Galeta coastal.

Efforts should be made to continue to locate different types of sites which may be more severe than either the established or experimental sites used in this investigation.

OBJECTIVE

The objective of this study was to determine the relative severity of selected mangrove swamps on the corrosion of steel.

¹ Portig, W. H., J. C. Bryan, and D. A. Dobbins, *Determination of Optimum Tropic Storage and Exposure Sites, Phase II: Patterns and Predictions of Tropic Materials Deterioration*, USATTC Report No. 7405001, May 1974.

² Sprouse, J. F., M. D. Neptune, and J. C. Bryan, *Determination of Optimum Tropic Storage and Exposure Sites, Report II: Empirical Data*, USATTC Report No. 7403001, March 1974.

SECTION 2. DETAILS OF INVESTIGATION

EXPOSURE SITES

A total of seven mangrove sites were chosen for this study. Five of these were located on the Atlantic side of the Isthmus and two on the Pacific side. For comparison purposes, a non-mangrove breakwater site on the Atlantic Coast was included. This Atlantic coastal site, called the "comparison site," was selected because of its known severity toward corrosion of steel caused by high levels of salt spray deposited on samples. A Pacific site was not selected because there is none in the Canal Zone with salt spray as heavy as that which is produced on the Atlantic Coast, the reason being that the fetch of general offshore winds is not sufficiently long to increase the salt content of the air to Atlantic Coast levels.

Figure 1 shows the geographical location of the eight sites.

The term *mangrove* is a common name given to a group of trees usually found in saltwater and brackish-water intertidal areas in the tropics and subtropics. At the Rodman Pacific site, approximately 50 percent of the tree species are mature *Pelliciera Rhizophorae*. Species comprising the other vegetation are mature specimens of *Rhizophora mangle* (Red mangrove) (45 percent) and *Avicennia nitida* (Black mangrove) (5 percent). At the Kobbe Pacific site, 100 percent of the vegetation was *Laguncularia racemosa* (White mangrove) in early maturity. Both sites have an open understory with only a few mangrove seedlings. This widely open understory is indicative of the relative maturity of trees in the area.

Mangrove species represented at the Atlantic exposure sites were as follows:

Table 1. Mangrove Species—Atlantic Site

<u>Site</u>	<u>Mangrove Species</u>
Coco Solo Mangrove A	<i>Avicennia nitida</i> (black mangrove) <i>Laguncularia racemosa</i> (white mangrove)
Coco Solo Mangrove B	<i>Rhizophora mangle</i> (red mangrove) <i>Pelliciera</i> <i>Rhizophora</i> and <i>Avicennia nitida</i>
Galeta Point Mangrove	<i>Rhizophora mangle</i>
Sherman Mangrove A	<i>Avicennia nitida</i>
Sherman Mangrove B	<i>Rhizophora mangle</i>

All Atlantic sites had an open understory occupied by only a few small seedlings of the predominant canopy species. Coco Solo Mangrove A had a few over-mature remnants from a previous mangrove forest. All major mangrove species were represented at one or more of the seven exposure sites.

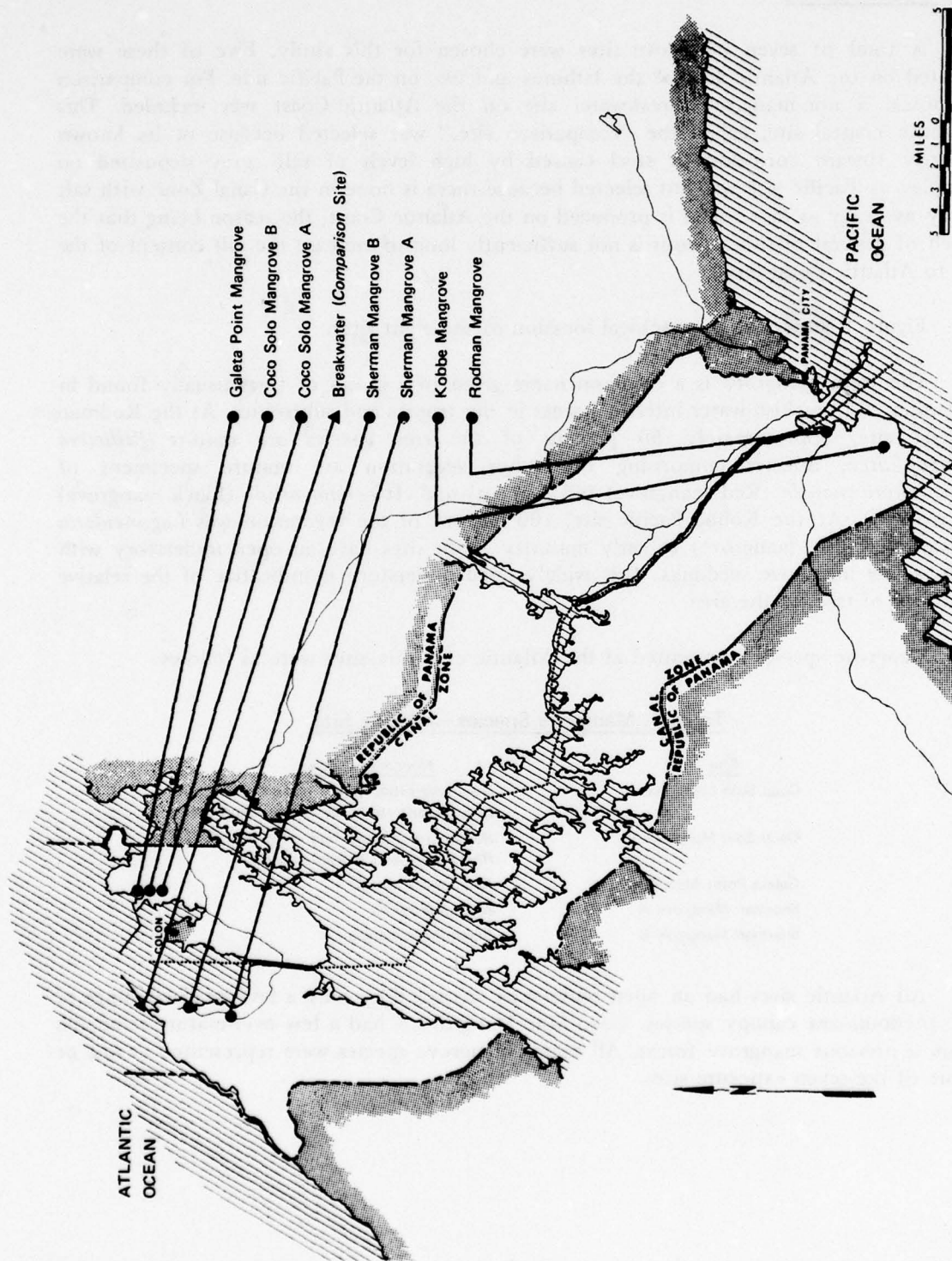


Figure 1. Geographical Location of Exposure Sites in the Canal Zone.

DATA COLLECTION

● **Steel Tensile Strength.** The exposure samples used in this investigation were mild steel shimstock, 0.01 inch thick, conforming to AISI 1006 carbon steel. The samples were emplaced in the form of strips, 1 inch wide, on racks 30° to the horizontal, similar to the exposure mode used in the *Optimum Tropic Exposure Sites* project.^{1,2} A total of 90 samples were exposed at each exposure site during each season. At weekly intervals, six samples were retrieved from each site and tested for tensile strength. This process continued until the last six samples were retrieved after 15 weeks of exposure. The periods of exposure were from 23 September 1973 to 9 January 1974 in the wet season, and from 31 January 1974 to 15 May 1974 in the dry season.

● **Water Run-Off Samples.** To explain site differences in corrosiveness toward metals, water samples were collected at each of the seven mangrove sites. The samples from each site were collected by attaching a funnel/bucket collection system to a mangrove tree, as shown in figure 2. Water samples were collected on a weekly basis during the rainy periods of both the wet and dry seasons, and returned to the chemistry laboratory for analyses. During periods of little or no rain, samples could not be collected because insufficient water accumulated in the samplers. The water samples were routinely analyzed for total ionic strength (conductivity in mho/cm), pH, and water soluble chloride concentration.

The conductivity measurement provided electrolytic strength of the water by electrochemical measure of total ionic concentration in the solution. This measurement is a good indicator of corrosiveness. Computations were made with a Barnstead model PM70-CB conductivity bridge using a model B-1 conductivity cell with a cell constant of 0.1. Hydrogen ion concentration measurements were performed with a Beckman 41263 glass electrode with a calomel reference electrode. Water soluble chloride measurements were completed by the manual mercuric nitrate titration method using diphenyl carbazone bromphenol blue indicator.

DATA ANALYSES

● **Degradation Model.** The measured tensile strength data were plotted against exposure time to determine the appropriate mathematical model to represent the degradation trend. Some of the plots suggested a curve of the form $y = a \exp(-b x^c)$ (where y = tensile strength, x = exposure time, and a , b , and c are empirical positive constants), which has as its shape, a quasi-linear decline and then a leveling off portion which becomes asymptotic to zero. However, most of the data revealed a more linear trend in the declination of tensile strength versus exposure time. The straight line was chosen as the degradation model for those data which were non-linear, since the downward trend during the first 90 to 95 percent loss of tensile strength was linear, and the leveling-off portion represented only a 5 to 10 percent value of original tensile strength. For all practical purposes this represents a totally degraded piece of steel.

¹ Ibid.

² Ibid.



a. One of Seven Mangrove Sites Chosen for Run-Off Sampling.



b. Close-Up of Funnel/Bucket Collection System.

Figure 2. Technique Used for Collection of Water Run-Off Samples.

The method of least-squares was used to determine the equations of the best fit lines for each set of data. These lines have been plotted with the raw data in figures A-1 through A-16 in appendix A. Also shown in these plots are the 95 percent upper and lower prediction limits about the best fit lines.*

● **Degradation Rate.** All regression lines shown in the figures of appendix A, have the form $y = a + bx$. Tables 2 and 3 list the eight sites in order of increasing degradation rates, and also give the two-sided 90-percent confidence intervals for the true rates of degradation. The right-hand columns in tables 2 and 3 indicate which degradation rates are not statistically different from one another. An overlapping of the upper limit of one site with the lower limit of another indicates that the differences shown could be chance occurrences. Conversely, if the interval of one site does not overlap with another, then the degradation rates are statistically different at the 0.1 level of significance, approximately, and are probably real differences.

Table 2. Degradation Rates—Wet Season
(kgs/week loss in tensile strength)

Site		Point Estimate (Average)	95% Lower Confidence Limit	95% Upper Confidence Limit	Remarks
Kobbe Mangrove	(P)	- 9.84	-12.6	- 7.06	} No Significant Difference ($\alpha \cong 0.1$)
Sherman Mangrove A	(A)	-17.2	-20.8	-13.6	
Rodman Mangrove	(P)	-21.1	-26.1	-16.0	
Sherman Mangrove B	(A)	-20.9	-25.5	-16.3	
Coco Solo Mangrove B	(A)	-22.5	-25.6	-19.4	
Breakwater (Comparison)	(A)	-47.1	-49.2	-44.9	
Galeta Point Mangrove	(A)	-47.1	-49.8	-44.3	
Coco Solo Mangrove A	(A)	-66.7	-72.9	-60.4	

LEGEND: (A) Indicates Atlantic site.
(P) Indicates Pacific site.

Table 3. Degradation Rates—Dry Season
(kgs/week loss in tensile strength)

Site		Point Estimate (Average)	95% Lower Confidence Limit	95% Upper Confidence Limit	Remarks
Kobbe Mangrove	(P)	- 2.60	- 4.26	- 0.94	} No Significant Difference ($\alpha \cong 0.1$)
Galeta Point Mangrove	(A)	- 3.59	- 5.24	- 1.95	
Rodman Mangrove	(P)	- 5.26	- 7.63	- 2.90	
Sherman Mangrove A	(A)	- 5.47	- 6.69	- 4.24	
Coco Solo Mangrove B	(A)	- 6.75	- 8.22	- 5.27	
Sherman Mangrove B	(A)	- 7.68	- 8.90	- 6.46	
Coco Solo Mangrove A	(A)	-42.4	-46.1	-38.8	
Breakwater (Comparison)	(A)	-91.5	-96.5	-86.5	

LEGEND: (A) Indicates Atlantic site.
(P) Indicates Pacific site.

* All statistical formulae are given in appendix B.

● **Expected Life.** The point at which the exposed steel reached a tensile strength of 300 kilograms (approximately 50 percent of original strength) was arbitrarily chosen as the time to failure, or expected life. From the equation $y = a + bx$, given in figures A-1 through A-16, the expected life, X_0 , was computed by setting $y = 300$. For purposes, again, of statistically comparing sites, the two-sided 90-percent confidence interval for expected life were computed from respective upper and lower prediction line formulae. Tables 4 and 5 give the results of this analysis. (Care should be used in interpreting tables 4 and 5. As can be seen, some of the expected lives extend beyond the duration of a wet or dry season. Hence, these tables cannot be used as true predictors of life expectancy but rather as a comparative guide to site severity.)

Table 4. Expected Life* of Steel—Wet Season

(in weeks)

Site		Point Estimate (Average)	95% Lower Confidence Limit	95% Upper Confidence Limit	Remarks
Kobbe Mangrove	(P)	29.7	17.8	45.4	} } } No Significant Difference ($\alpha \cong 0.1$)
Sherman Mangrove A	(A)	18.4	9.8	27.9	
Rodman Mangrove	(P)	15.9	6.0	26.7	
Sherman Mangrove B	(A)	12.8	3.6	22.5	
Coco Solo Mangrove B	(A)	12.2	6.5	18.1	
Breakwater (Comparison)	(A)	6.7	5.2	8.2	
Galeta Point Mangrove	(A)	5.2	3.5	6.9	
Coco Solo Mangrove A	(A)	3.4	1.9	4.9	

* Time required for tensile strength to degrade to 300 kilograms (approximately 50 percent of original strength).

LEGEND: (A) Indicates Atlantic site.
(P) Indicates Pacific site.

Table 5. Expected Life* of Steel—Dry Season

(in weeks)

Site		Point Estimate (Average)	95% Lower Confidence Limit	95% Upper Confidence Limit	Remarks
Kobbe Mangrove	(P)	97.0	56.4	260.1	} } } No Significant Difference ($\alpha \cong 0.1$)
Galeta Point Mangrove	(A)	76.3	49.6	139.1	
Rodman Mangrove	(P)	42.5	22.9	79.6	
Sherman Mangrove A	(A)	51.0	39.5	67.2	
Coco Solo Mangrove B	(A)	40.5	30.3	54.0	
Sherman Mangrove B	(A)	37.1	29.7	46.0	
Coco Solo Mangrove A	(A)	7.9	4.4	11.4	
Breakwater (Comparison)	(A)	2.9	2.4	3.5	

* Time required for tensile strength to degrade to 300 kilograms (approximately 50 percent of original strength).

LEGEND: (A) Indicates Atlantic site.
(P) Indicates Pacific site.

● **Analysis of Water Samples.** To explain the differences in degradation rates experienced at the exposure sites, the water samples collected were analyzed for conductivity, chloride concentration, and pH. Table 6 shows the results of this analysis for samples collected during the wet season. The sites are listed in the same order as in table 2. The pH values are not shown because essentially no differences were seen in the water samples from the different sites; all values ranged from 6.0 to 6.5.

Table 6. Average Electrolyte Strength of Water Run-off—Wet Season

Site		Conductivity (mho/cm)	Chloride (ppm)
Kobbe Mangrove	(P)	7.72×10^{-5}	18.0
Sherman Mangrove A	(A)	8.91×10^{-5}	29.1
Rodman Mangrove	(P)	1.00×10^{-4}	26.2
Sherman Mangrove B	(A)	1.00×10^{-4}	17.2
Coco Solo Mangrove B	(A)	1.29×10^{-4}	49.5
Galeta Point Mangrove	(A)	1.02×10^{-4}	34.6
Coco Solc Mangrove A	(A)	3.80×10^{-4}	221.2

LEGEND: (A) Indicates Atlantic site.
(P) Indicates Pacific site.

Examination of the chloride concentrations shown in table 6 reveals little or no correlation with the degradation rates shown in table 2. This is demonstrated by the fact that the salts in the water samples derive their origin not only from ambient saltfall (primarily sodium chloride) but also from exudations from the mangrove trees themselves (other types of salts). Most of the water samples collected at the mangrove sites were yellow in color and upon evaporation yielded a brownish-yellow deposit. Small quantities of this deposit were pressed into KBr pellets for infrared analyses. The analysis showed the presence of only inorganic salts—primarily ammonium sulfate. Wet chemical tests confirmed the presence of ammonium and sulfate ions.

An increase in the concentration of ionic species in solution causes an increase in the solution conductivity which enhances metal corrosion. Comparison of the conductivity values in table 6 with the degradation rates in table 2 gives nearly the same order of site ranks based on increasing conductivity—Galeta Point mangrove being the exception. Therefore, the presence of water soluble salts in differing concentrations explains most of the difference in corrosiveness between sites. A linear correlation was performed using the conductivity measurements as predictors of the degradation rates (see appendix B). The correlation coefficient was $r = -.84$, and $r^2 = .71$. Hence, about 71 percent of the variation in degradation rates between sites is associated with the conductivity measurements.

Galeta Point Mangrove site is the only exposure site which seems to fall out of place when comparing conductivity versus degradation rate. (The uniqueness of the Galeta site is discussed later.) Eliminating this site from the linear correlation routine, $r = .99$ and $r^2 = .98$, or 98 percent of the variation in degradation rates, are associated with the conductivity of the water run-off samples.

VARIATIONS IN EXPOSURE SEASONS AND SITES

● **Wet versus Dry Season.** The increased amount of degradation during the wet season is apparent in all but the Breakwater comparison site. Statistical analysis of the wet versus dry season degradation rates shows that a significant difference exists within each site.

This is easily explained in that the primary salt in the mangrove water run-off was sodium chloride with traces of ammonium sulfate. The majority of corrosion products formed on mild steel would therefore be water soluble compounds such as FeCl_2 and hydrated ferrous sulfate instead of non-soluble $\text{Fe}(\text{OH})_2$ and $\text{Fe}(\text{OH})_3$. The majority of the water soluble corrosion products formed would be washed away by heavy rainfall in the wet season because more run-off from the mangrove trees reach the samples. As the surface corrosion products were washed away, a new metal surface would be exposed and the rate of corrosion would increase.

Conversely, in the dry season, the water soluble corrosion products were washed off to a lesser degree because of less rainfall. The accumulated corrosion products then acted as a protective barrier, thus reducing further corrosion.

The rains of the wet season had a cleansing effect on the Breakwater comparison site samples; i.e., by washing away the salt-spray buildup with *fresh* water before corrosion could occur. A two-fold increase in the degradation rate at the Breakwater site in the dry season was brought about by increased salt spray from the Caribbean Sea caused by high northerly winds during that period.

Copson³, in a study of the mechanism of rusting, found that the corrosion rate of steel depended on the quality and quantity of water in contact with the steel. The quality was affected by pollution, solubility of corrosion products, and by the washing effect of rain; the quantity was affected by the amount of rain, dew, the degree of shelter, and the porosity of the rust. Rain played a dual role—accelerating corrosion by providing the necessary moisture for electrolyte formation or retarding corrosion by washing away corrosive contaminants.

Also during the *Optimum Tropic Exposure Sites* project¹, a higher wet season tensile strength loss was noted at the coastal, open, and, to a lesser degree, the forest sites. This accelerated degradation was not noted, however, in the sheltered sites where the steel samples were not exposed to falling rain.

A rank-difference coefficient of correlation was computed to compare the mangrove sites by degradation rates between wet and dry seasons. The correlation coefficient was .57, which indicates that the sites maintained only moderately similar order from wet to dry season. A closer observation of the order of ranking shows this order change was caused by the large difference in the rank of the Galeta Point Mangrove site between seasons. Galeta Point placed second from the bottom during the wet season, and second

³ Copson, H. R., *A Theory on the Mechanism of Rusting of Low Alloy Steels in the Atmosphere*, ASTM Proceedings, 45: 554-590, 1945.

¹ Op cit.

from the top during the dry season (see tables 2 and 3). Omitting this site, the rank-difference correlation coefficient for the remaining six sites was .89, i.e., high correlation between seasons.

- **Galeta Point Mangrove.** The Galeta site has been shown to be an anomaly in the ranking of sites by severity. The dry season ranking and the wet season conductivity and chloride measurements make the degradation rate during the wet season appear too high. However, looking at figure A-7, the degradation trend seems well established. The reasons for this are not known. It indicates that all factors affecting steel corrosion in the mangrove forests have not been defined.

- **Coco Solo Mangrove A.** The degradation rate of the Coco Solo Mangrove A site was more severe than the other mangrove sites in both seasons (see tables 2 and 3). A current hypothesis as to the severity of this site in the dry season is that it was very humid, to the point of causing water drippage from the mangrove leaves. This higher humidity was brought about through evaporation from the swamp since it was better protected against wind than the other sites. The drippage added to the corrosion process in the same manner as did the rains of the wet season.

Although this hypothesis might explain the dry season severity, it does not explain why the salt and conductivity measurements were much higher than the other sites. Some leaves from the predominate species at each mangrove site have been collected and laboratory-tested for salt content during the preliminary investigations for another USATTC project. Although incomplete at this time, the leaves of the Coco Solo Mangrove A site appear to contain a salt concentration from 3 to 16 times greater than those in the other sites. Therefore, it appears that the conductivity and salt concentration measurements at the Coco Solo Mangrove A site were more a function of the exuded salt from the mangroves than salt spray from the ocean.

- **Pacific Sites.** The degradation rate of the Kobbe Pacific Mangrove site was less severe than any other site during either season. The cause for Kobbe's relatively mild severity is shown by the low conductivity measurements presented in table 6. A current hypothesis is that the salt in the rainwater run-off from the mangrove trees is a function of the species of tree and the salt content of the water about the root structure. The hypothesis seems confirmed for this site because it is located where only the highest of Pacific high tides bring saltwater into it.

The Rodman Pacific site was wetter than Kobbe. The Rodman mangrove site was flooded twice daily with the incoming Pacific tides, which probably accounted for the statistical difference in degradation rates between Rodman and Kobbe during the wet season. The relatively mild severity of most sites during the dry season (see tables 3 and 5) should therefore account for the lack of differences between Kobbe and Rodman during the drier months.

The generally milder severity of the Pacific sites, as compared with the Atlantic sites, was attributed to the higher salt concentration of the air on the Atlantic side caused by higher winds and the greater tidal change on the Pacific side.

CONCLUSIONS

- The high degradation rate of the steel samples in the wet season is caused by a higher concentration of electrolytes in the rainwater run-off. The majority of the corrosion products are washed away by heavy rainfall, thereby exposing a new layer of steel that undergoes further corrosion. Conversely, a semipassivity on the surface of the samples in the dry season is developed because the water soluble corrosion products are not washed away. The wet season is therefore significantly more severe to mangrove exposed steel.

- The high conductivity of the water run-off is well correlated to the tensile strength loss. This high conductivity is caused primarily by water soluble salts found in the water run-off samples. These salts form on the leaves and branches of the mangrove trees by exudation and from saltfall onto the canopy. The amount of salt exuded by the mangrove tree appears to be a function of the species of tree, the salt content of the soil, and the amount of water about the root structure.

- The expected life of the steel samples exposed at mangrove sites ranged from 97 weeks at the Kobbe Mangrove (Pacific) site during the dry season, to only 3.4 weeks at the Coco Solo Mangrove A (Atlantic) site during the wet season.

- The degradation rates ranges from 2.6 kgs/week at the Kobbe Mangrove site during the dry season, to 66.7 kgs/week at the Coco Solo Mangrove A site during the wet season.

- Mangrove swamps are not universally severe to steel and must therefore be selected carefully in planning tropic exposure tests.

- The Coco Solo Mangrove A exposure site provides the most accelerated mangrove exposure test because of its uniquely high corrosiveness.

- The breakwater site has a two-fold increase in metal degradation during the dry season.

RECOMMENDATION. This Center recommends that:

- A Test Operations Procedure (TOP) not be developed based on the results of this investigation.

APPENDIX A. DATA PLOTS AND PREDICTION CURVES

Figures A-1 through A-16 of this appendix illustrate the raw data distribution for each exposure site in both wet and dry seasons in the Canal Zone.

The solid line through the measured data is the best fit *least-squares* straight line which is bounded by the 95-percent upper and lower prediction limits represented by dashed curves. Formulae for the lines are given on the respective plots and have the form $y = a + bx$, where y and a are kilograms of tensile strength, b is kilograms/week, and x is exposure time in weeks. Formulae used to derive the prediction limits are given in appendix B.

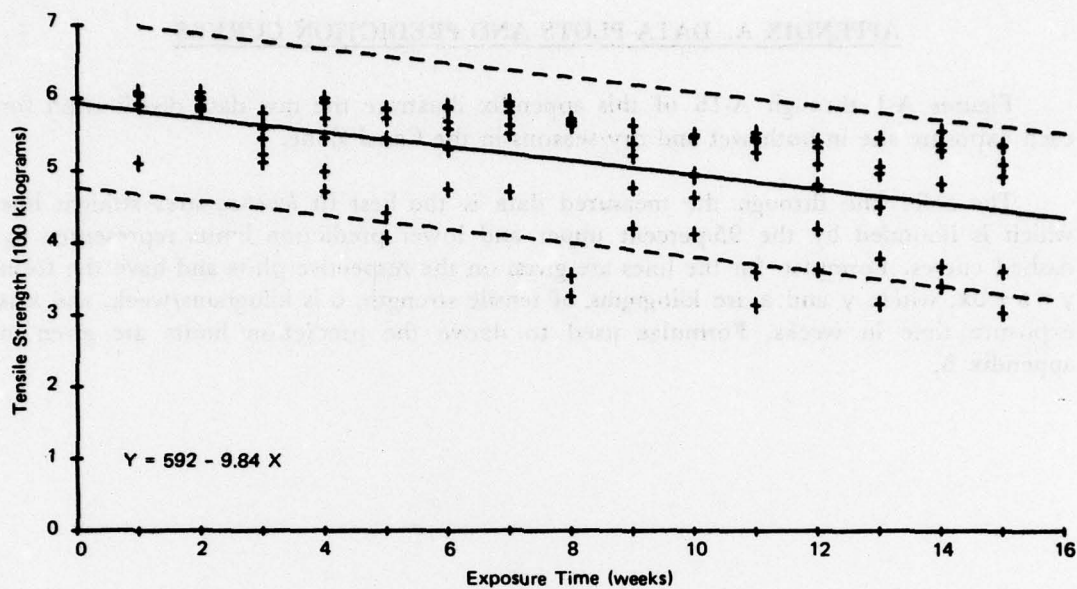


Figure A-1. Steel Strength—Kobbe Mangrove—Wet Season.

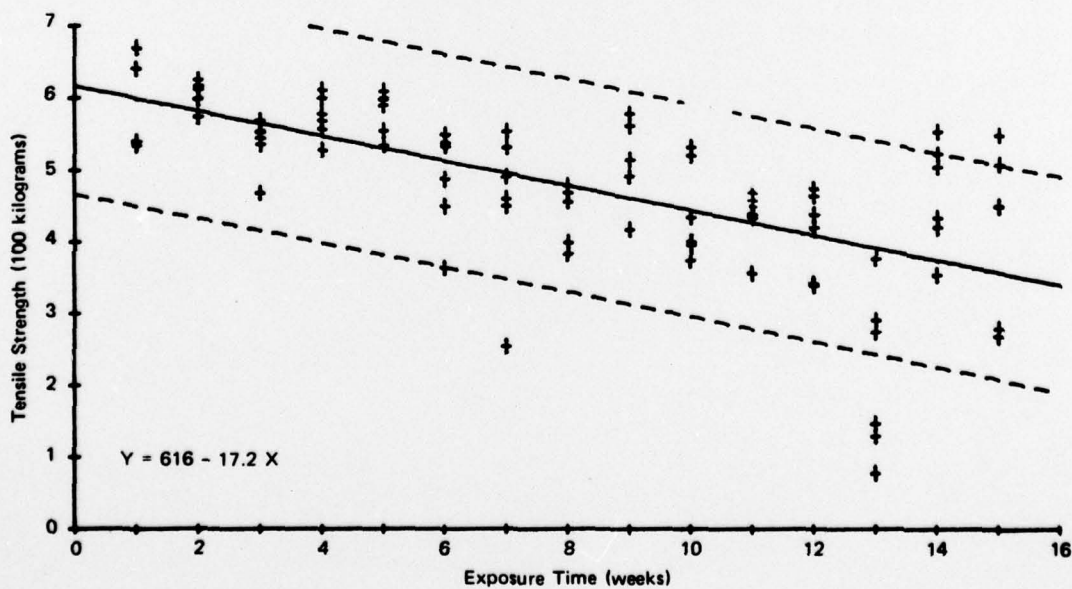


Figure A-2. Steel Strength—Sherman Mangrove A—Wet Season.

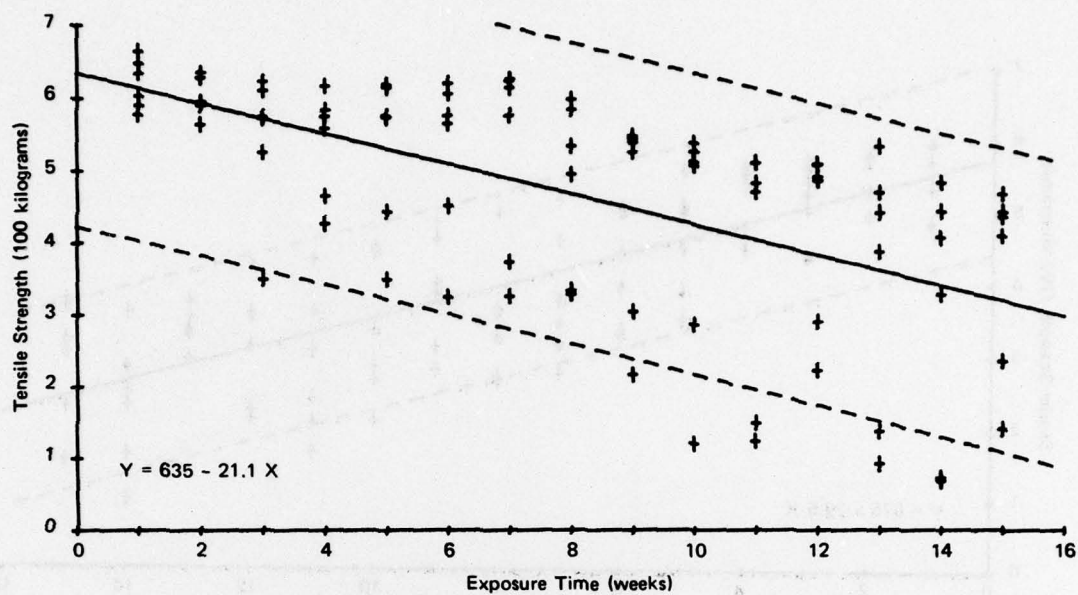


Figure A-3. Steel Strength—Rodman Mangrove—Wet Season.

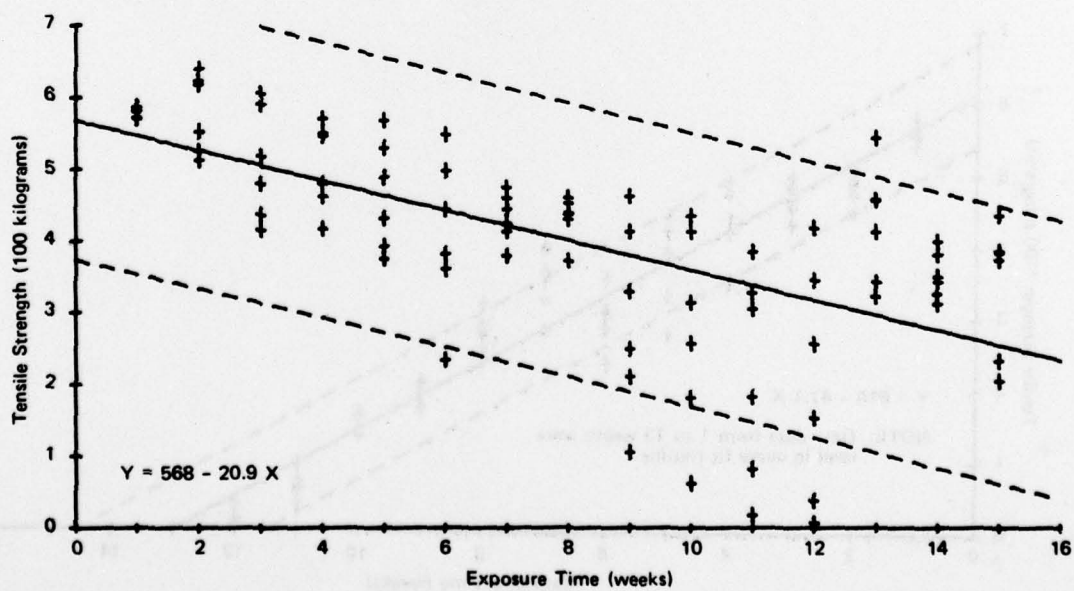


Figure A-4. Steel Strength—Sherman Mangrove B—Wet Season.

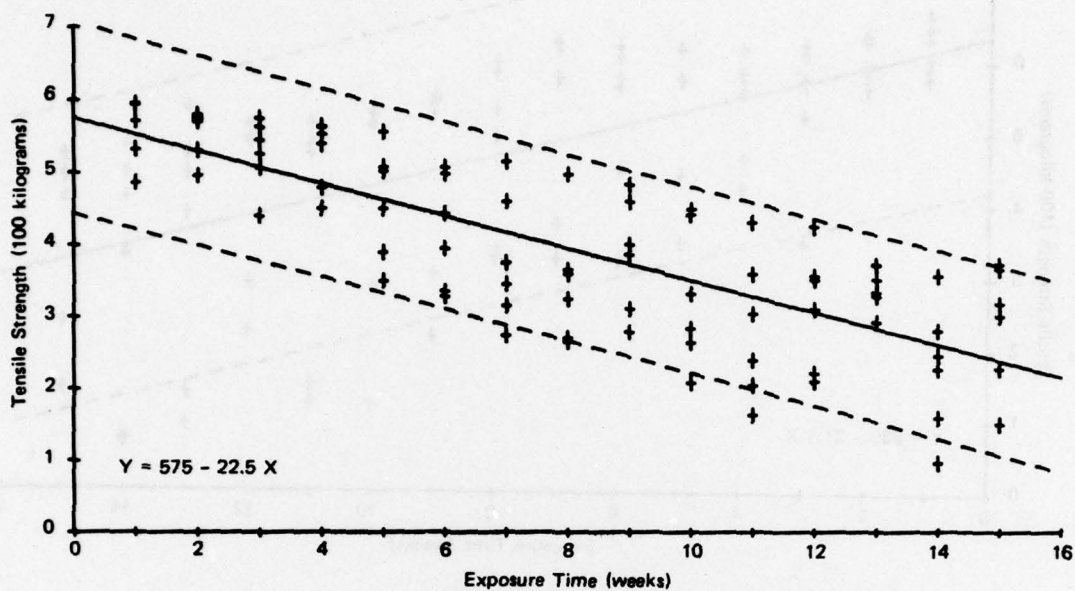


Figure A-5. Steel Strength—Coco Solo Mangrove B—Wet Season.

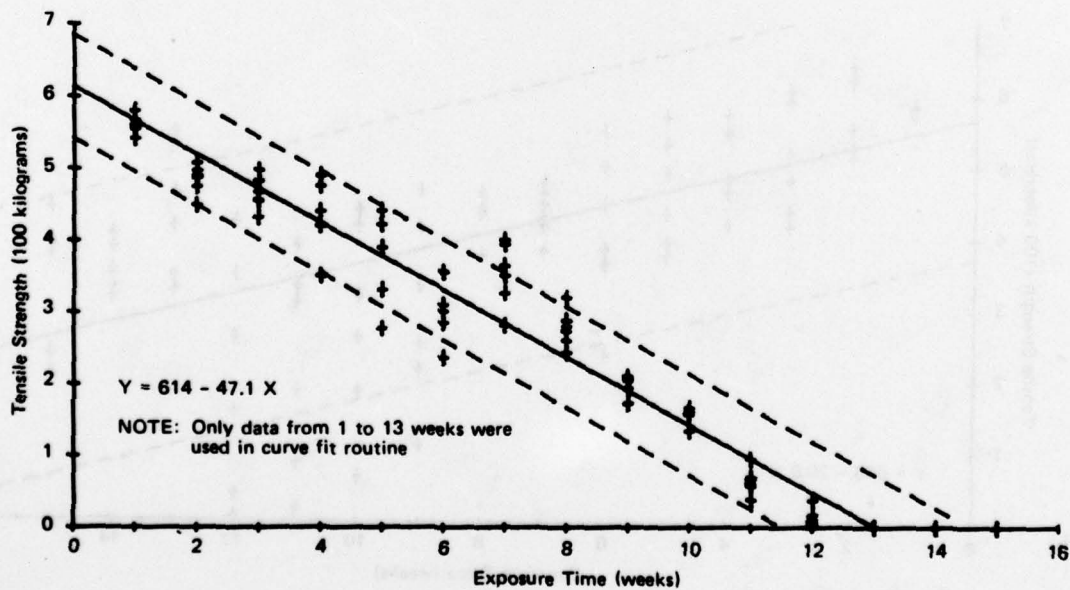


Figure A-6. Steel Strength—Breakwater—Wet Season.

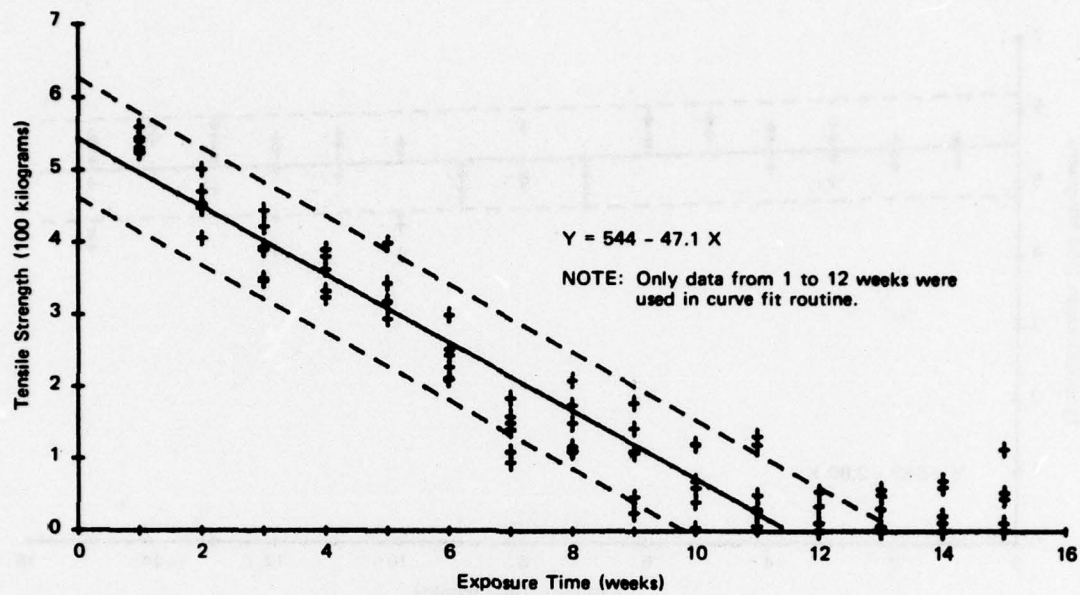


Figure A-7. Steel Strength—Galeta Point Mangrove—Wet Season.

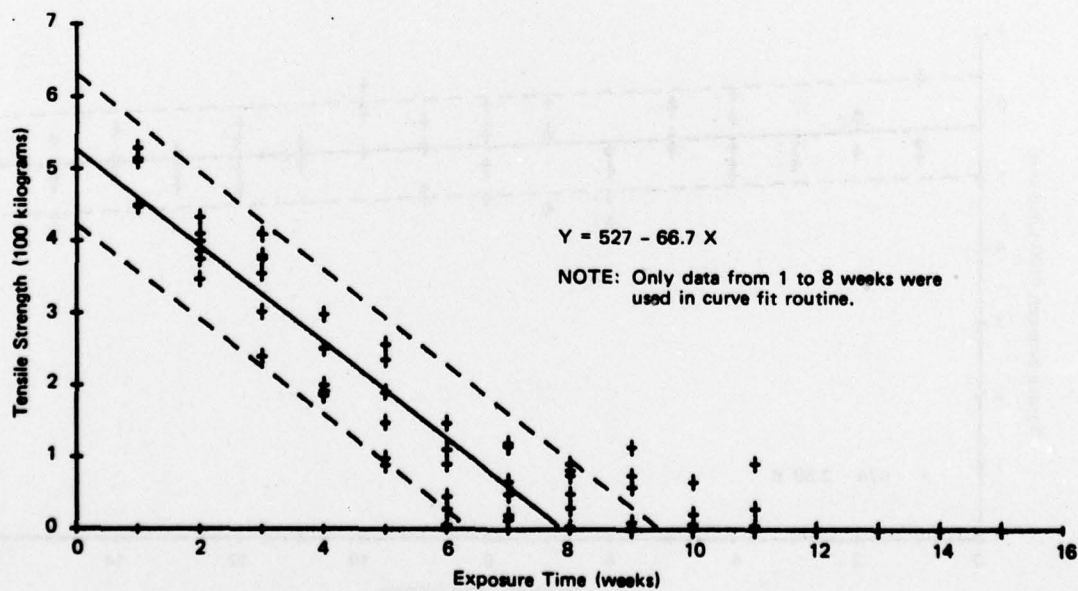


Figure A-8. Steel Strength—Coco Solo Mangrove A—Wet Season.

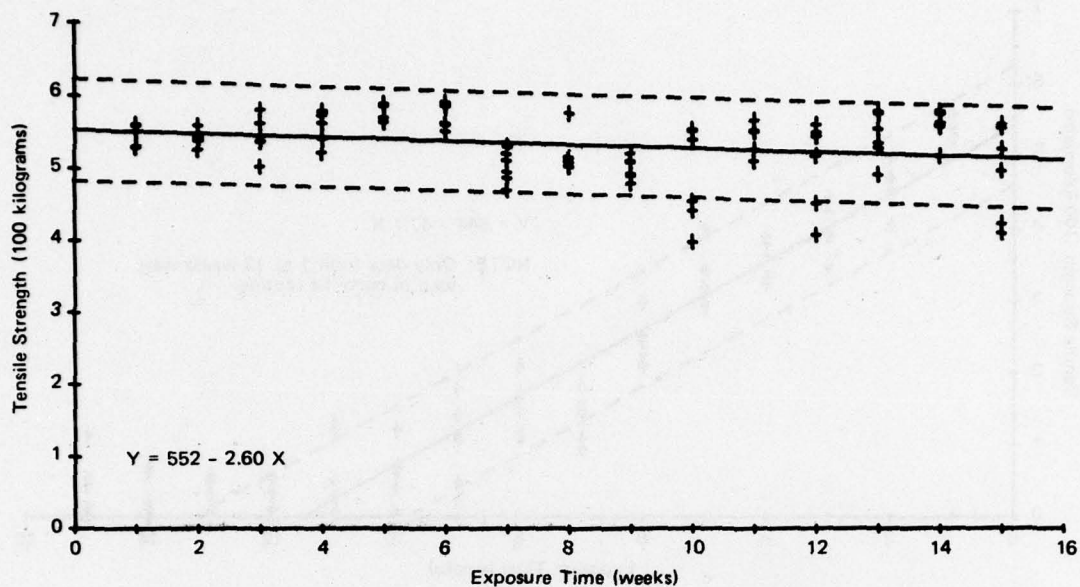


Figure A-9. Steel Strength—Kobbe Mangrove—Dry Season.

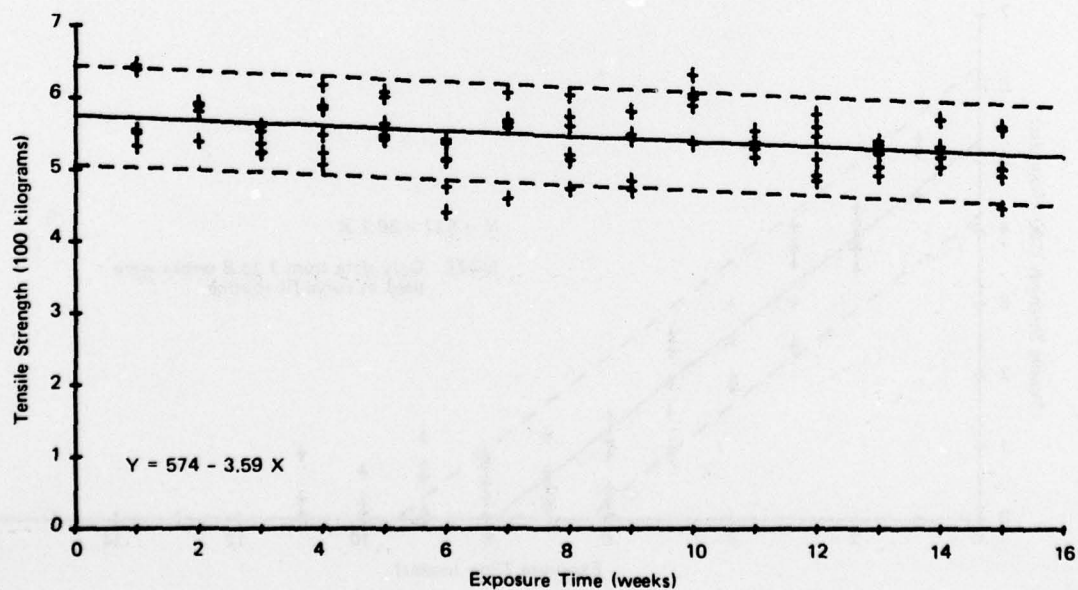


Figure A-10. Steel Strength—Galeta Point Mangrove—Dry Season.

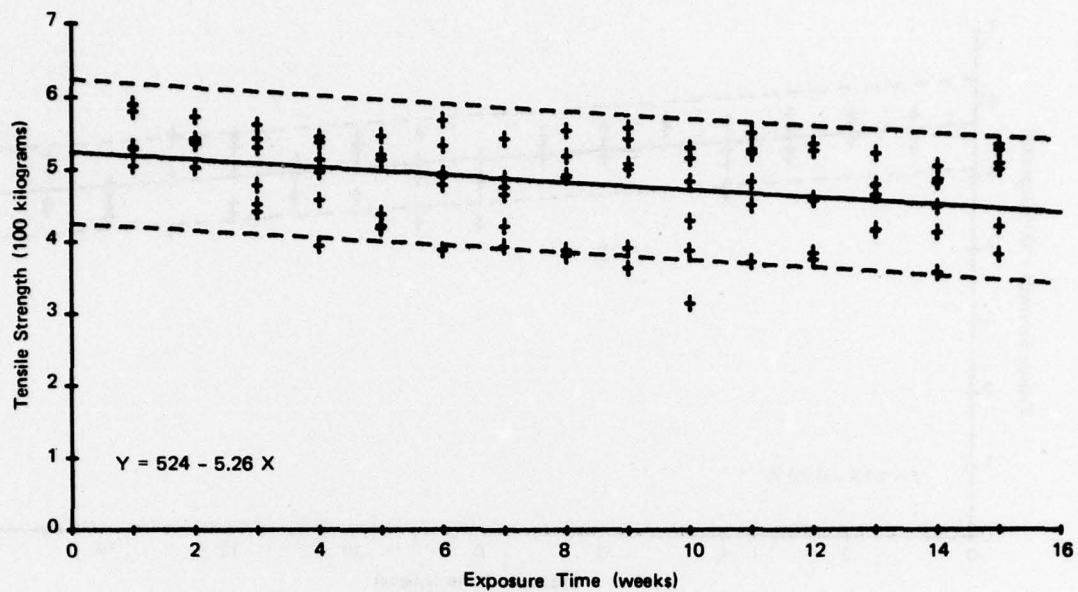


Figure A-11. Steel Strength—Rodman Mangrove—Dry Season.

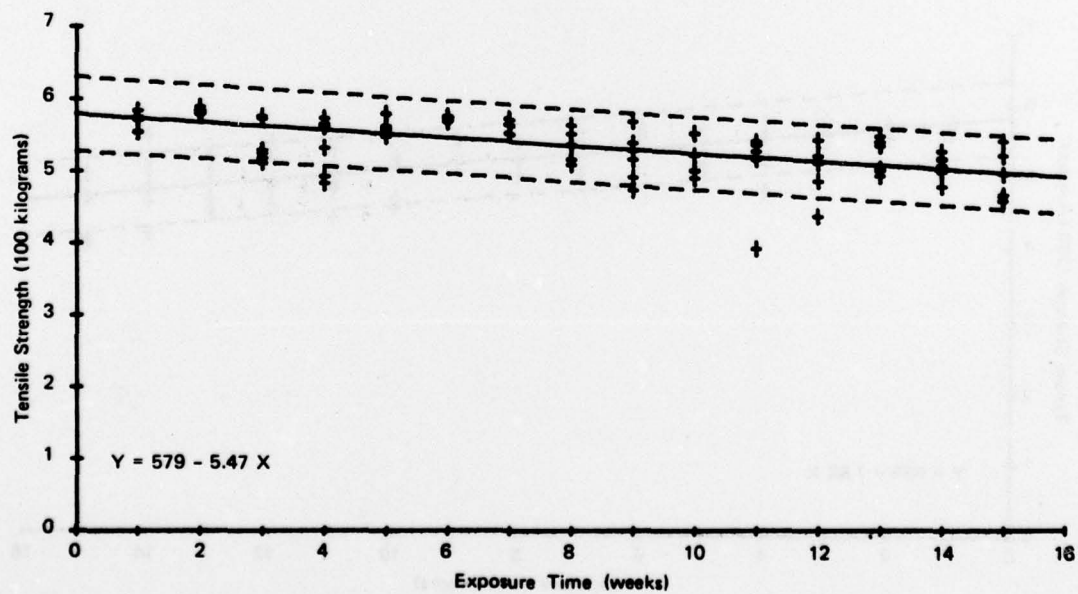


Figure A-12. Steel Strength—Sherman Mangrove A—Dry Season.

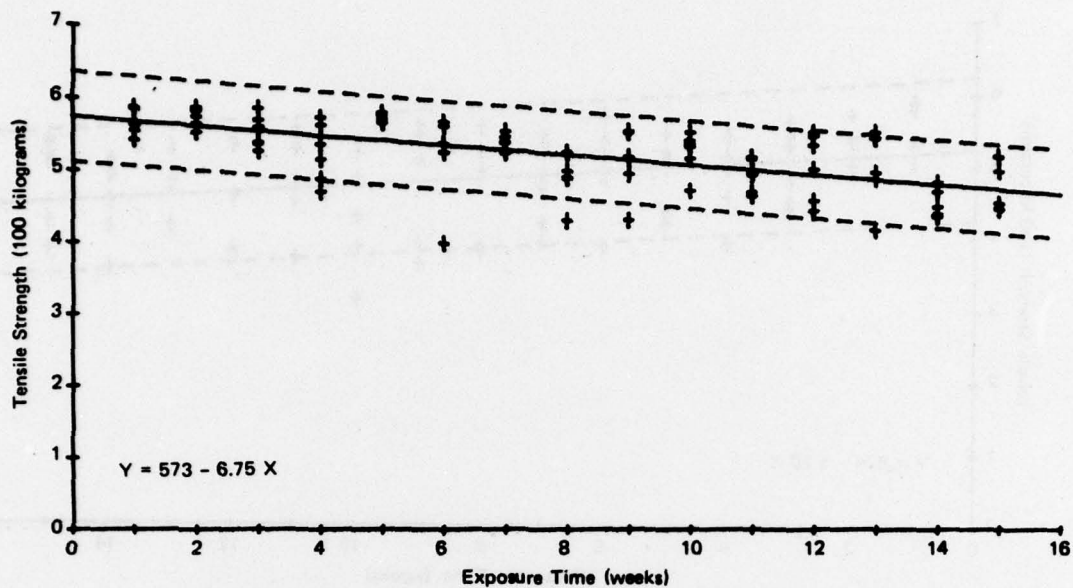


Figure A-13. Steel Strength—Coco Solo Mangrove B—Dry Season.

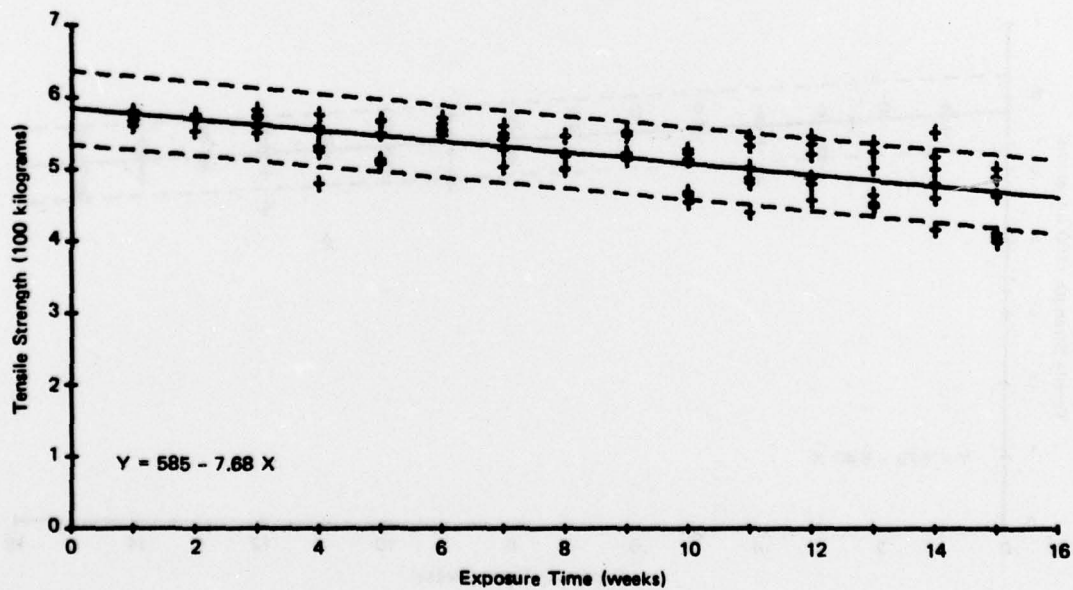


Figure A-14. Steel Strength—Sherman Mangrove B—Dry Season.

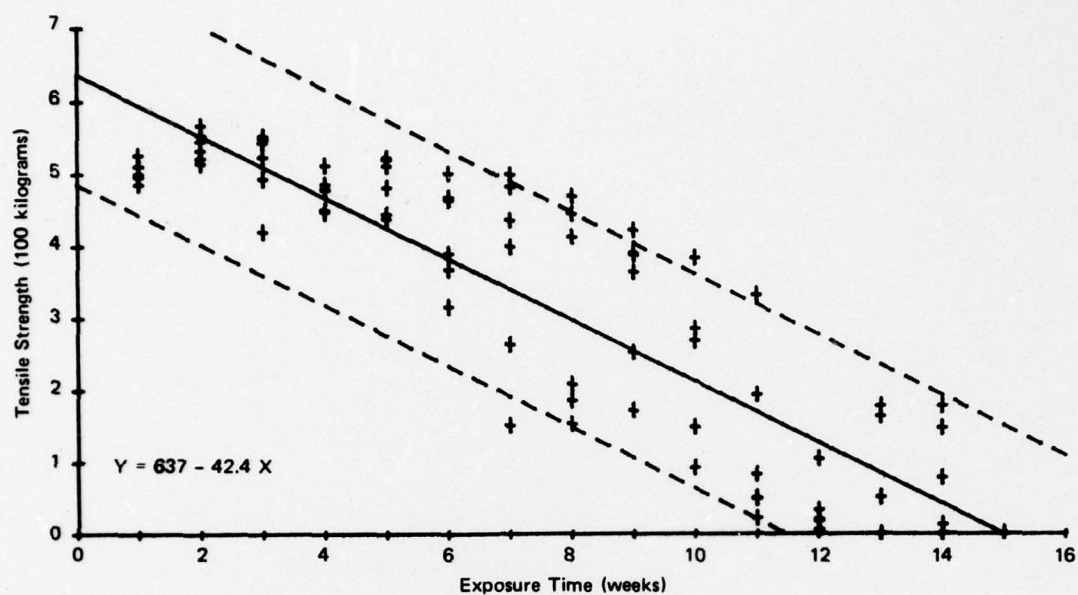


Figure A-15. Steel Strength—Coco Solo Mangrove A—Dry Season.

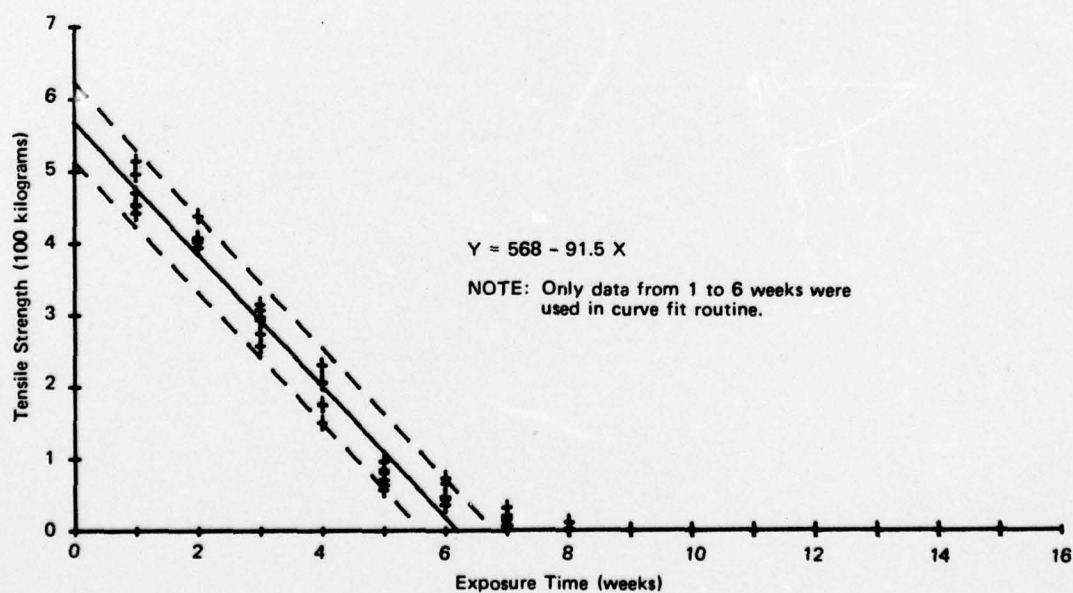


Figure A-16. Steel Strength—Breakwater—Dry Season.

APPENDIX B. STATISTICAL FORMULAE⁴

Given a set of data (X_i, Y_i) , $i = 1, 2, 3, \dots, n$, where X_i is exposure time in weeks and Y_i is the measured steel tensile strength in kilograms, the coefficients a and b of the formula

$$Y = a + bX$$

are computed through normal least-squares procedures by the formula

$$b = \frac{(\sum_i X_i)(\sum_i Y_i) - n\sum_i X_i Y_i}{(\sum_i X_i)(\sum_i X_i) - n\sum_i X_i^2}, \text{ and}$$

$$a = \frac{\sum_i Y_i - b\sum_i X_i}{n}$$

The 95-percent upper and lower confidence limits for the degradation rate, b , are given by the formula

$$b \pm \frac{t(S_{Y,X})}{S_X \sqrt{n-2}}$$

where t is the Student's t -statistic at the $\alpha = 0.05$ level of significance for $n-2$ degrees of freedom,

$$S_{Y,X} = \sqrt{\frac{\sum_i Y_i^2 - a\sum_i Y_i - b\sum_i X_i Y_i}{n}}, \text{ and}$$

$$S_X = \sqrt{\frac{\sum_i (X_i - \bar{X})^2}{n}}, \text{ where}$$

$$\bar{X} = \frac{1}{n} \sum_i X_i.$$

The prediction interval (represented by dashed curves in figures A-1 through A-16) is represented by the 95-percent upper and lower prediction limits of true tensile strength versus exposure time by the formula

$$Y = a + bX \pm tS_{Y,X} \sqrt{\frac{n+1 + \left(\frac{X - \bar{X}}{S_X}\right)^2}{n-2}}$$

Computation for Rank-Difference Coefficient of Correlation⁵

Given N corresponding pairs of measured items (degradation rates), where (U_i, V_i) , $i = 1, 2, 3, \dots, N$, are the corresponding rank numbers, then the rank-difference coefficient of correlation is given by the formula

$$r = 1 - \frac{6\sum_i (U_i - V_i)^2}{N(N^2 - 1)}, -1 \leq r \leq 1.$$

⁴ Spiegel, M. R., *Theory and Problems of Statistics*, McGraw-Hill Book Company, New York, October 1961.

⁵ Hodman, C. D., S. M. Selby, and R. C. Weast, *Standard Mathematical Tables, Twelfth Edition*, Chemical Rubber Publishing Company, Cleveland, Ohio, 1960.

APPENDIX C. REFERENCES

1. Portig, W. H., J. C. Bryan, and D. A. Dobbins, *Determination of Optimum Tropic Storage and Exposure Sites, Phase II: Patterns and Predictions of Tropic Materials Deterioration*, USATTC Report No. 7405001, TECOM Project No. 9 CO 009 000 005, US Army Tropic Test Center, Fort Clayton, CZ, May 1974, AD A005018.
2. Sprouse, J. F., M. D. Neptune, and J. C. Bryan, *Determination of Optimum Tropic Storage and Exposure Sites, Report II: Empirical Data*, USATTC Report No. 7403001, TECOM Project No. 9 CO 009 000 006, US Army Tropic Test Center, Fort Clayton, CZ, March 1974, AD A005017.
3. Copson, H. R., *A Theory on the Mechanism of Rusting of Low Alloy Steels in the Atmosphere*, ASTM Proceedings, 45: 554-590, 1945.
4. Spiegel, M. R., *Theory and Problems of Statistics*, McGraw-Hill Book Company, New York, October 1961.
5. Hodman, C. D., S. M. Selby, and R. C. Weast, *Standard Mathematical Tables, Twelfth Edition*, Chemical Rubber Publishing Company, Cleveland, OH, 1960.